

# Characterisation and differentiation of kerogens by pyrolytic and chemical degradation techniques

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Received 5 May 2000; accepted 27 October 2000

## Abstract

The structural characterization of a set of kerogen concentrates belonging to the three well differentiated conventional main types (I, II, III) has been undertaken by pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS) both in the absence and presence of tetramethylammonium hydroxide (TMAH). The results obtained have been compared to the structural features as discerned by chemical degradative methods (KMnO<sub>4</sub> or RuO<sub>4</sub> oxidation, hydrolysis with phase transfer catalyst and transalkylation reactions) and solid state <sup>13</sup>C-NMR spectroscopy. The compounds released upon conventional pyrolysis were mainly saturated and olefinic hydrocarbons for the type I and II kerogen samples, whereas aromatic compounds were predominant in the kerogen of type III, in agreement with KMnO<sub>4</sub> oxidation data and the NMR spectra. Pyrolysis/TMAH released relatively high amounts of saturated and unsaturated unbranched mono- and dicarboxylic acids (as their methyl esters) from all the samples, as well as minor amounts of aromatic acids (as their methyl esters), which indicates that considerable amounts of functionalized compounds are bound to the macromolecular structure via ester or ether linkages. Overall, Py/TMAH and chemical degradations give complementary results concerning the chemical nature of the released fatty acid series identified. © 2001 Elsevier Science B.V. All rights reserved.

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**Keywords:** Kerogen; Pyrolysis; Pyrolysis-methylation; Tetrametylammonium hydroxyde (TMAH); Chemical degradative techniques; CPMAS  $^{13}\text{C}$ -NMR

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## 1. Introduction

In spite of the great progress made in the last years, the determination of the specific origin of the various conventional types of kerogens and their formation pathways are still an important subject of organic geochemical research. For this purpose, a detailed elucidation of the structural characteristics of kerogens, which is far from being solved due to the inherent intractability and recalcitrant nature of these complex polycondensed and polyfunctional materials is required.

Kerogens are known to correspond to cross-linked macromolecular systems composed by the combination of resistant bio- and geomacromolecules and incorporated low-molecular-weight biomolecules. Their formation can be explained by classical depolymerisation/recondensation and/or selective preservation models [1–3]. They can be structurally viewed as three-dimensional macromolecules formed by nuclei that are cross-linked by chain-like bridges. Both nuclei and bridges may bear functional groups and lipids may be trapped within the structure. There are a variety of bridging structures between the nuclei, including aliphatic chains (linear and branched), O- or S-containing functional groups, and combinations of the two.

Structural studies of kerogen have been approached by a wide array of degradative and non-degradative analytical techniques [4], and references therein. The former include wet chemical degradation procedures and analytical pyrolysis, which have been shown to produce lower-molecular-mass compounds that reflect the composition of the original polymer. Due to the heterogeneity and the complexity of kerogens, different methods must be used complementarily to assess their structure. Such a strategy is needed to avoid controversial information and misinterpretations, and to precise some mechanisms occurring on chemical or thermal degradation.

Analytical pyrolysis (Py), in combination with gas chromatography (Py–GC), mass spectrometry (Py–MS) and gas chromatography/mass spectrometry (Py–GC/MS), has been one of the most widely used methods for routine molecular characterization and qualitative typing of kerogens during the last two decades [5–13]. In this paper we compare the structural information gained by applying pyrolytic techniques to a set of kerogen samples from different sources, with that previously obtained by the group of Prof. Amblès using different oxidative procedures such as multistep alkaline permanganate degradation [14–17], transalkylation with  $\text{CF}_3\text{SO}_3\text{H}$ /benzene [18–20], hydrolysis with a phase transfer catalyst — PTC — [18,19,21] and ruthenium tetroxide oxidation [20]. The kerogen samples have also been characterized by high-resolution  $^{13}\text{C}$ -NMR spectroscopy, a non-destructive approach which provides information on the kerogen structures as a whole.

Py–GC/MS has been performed both in the presence and absence of tetramethylammonium hydroxide (TMAH). The former pyrolytic approach, described as a thermally assisted hydrolysis and alkylation and/or pyrolysis–methylation [22] has been widely used in the last years for the characterization of bio- and geopolymers [23,24] including kerogens from different origins [12,25,26]. The study by pyrolysis–methylation will specifically provide information on the polar moieties bounded to the macromolecular structure of kerogens through ester and ether linkages since it yields derivatized products which are more amenable to GC than are their underivatized analogs.

## 2. Experimental

The samples selected for this study were two kerogens of Type I (Irati and Aleksinac), two of Type II (Mesnil/Vair and Donnemarie) and one of Type III (Mannville shale). Details on their origin and geochemical characteristics were published elsewhere [14–21].

The kerogen concentrates were prepared by treatment of the powdered shales with hydrochloric acid (1:4) at 70°C and then with hydrofluoric/hydrochloric acids (1:1), followed by a 60 h Soxhlet extraction of the washed (boric acid and water) and dried residues with an azeotropic mixture of benzene and methanol.

### 2.1. $^{13}\text{C}$ -NMR spectroscopy

Solid-state  $^{13}\text{C}$ -NMR spectra were acquired at 25.1 MHz with a Bruker MSL 100 spectrometer (2.3 Tesla) with the cross-polarization/magic angle spinning (CPMAS) technique. For each spectrum, 1000 free induction decays were accumulated. The pulse repetition rate was set to 5 s, and the contact time was 1 ms. The spectral width was 37.5 kHz and the acquisition time was 0.016 s. The MAS was performed at 4 kHz. The chemical shift range of the NMR spectra were referred to tetramethylsilane (= 0 ppm). Under these conditions, the NMR technique provides quantitative integration values in the different spectral regions [27].

### 2.2. Curie-point pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS)

Py–GC/MS analyses were performed using a Horizon Instruments Curie-point pyrolyser attached to a Varian Saturn 2000 Gas Chromatograph–Mass Spectrometer. The samples were deposited on pure iron wires with a Curie temperature of 770°C. The interface temperature of the pyrolysis unit was set at 250°C and the pyrolysis time was 5 s. For pyrolysis–methylation the samples were moistened with 10–20  $\mu\text{l}$  of TMAH (25% methanol solution) and deposited on ferromagnetic wires with a Curie temperature of 510°C. In both cases the GC oven was programmed from 50 to 100°C at 32°C/min and then up to 320°C at a rate of 6°C/min. The injector, equipped with a liquid carbon dioxide cryogenic unit, was temperature programmed from –30°C (1 min) to 300 at 200°C/min, while the GC–MS

interface was kept at 300°C. Separation was achieved using a fused-silica capillary column (25 m × 0.32 mm) coated with CPSil-5 (film thickness 0.4 μm) and helium was used as the carrier gas. Compound identification was based on mass spectral data and relative retention times. Relative contents of the different pyrolysis products were calculated on the basis on peak area. The total ion chromatograms were normalized on a basis of total signal intensity to correct for differences in sample size.

### 3. Results and discussion

The total ion chromatograms of the pyrolyzates obtained from the different kerogens by conventional Curie-point flash Py–GC/MS are shown in Fig. 1. The identities of the main pyrolysis compounds produced are marked on the peaks. The lack of similarity among the patterns suggests that significant structural differences are evident between kerogens of different or even the same conventional type.

In agreement with previous findings [5–10], the pyrolysates are progressively enriched in aromatic compounds as the maturity of the samples increases. This trend also closely resembles that depicted by the  $^{13}\text{C}$ -NMR spectra shown in Fig. 2. The different Py–GC/MS patterns for the two Paris basin kerogens (Donnemarie and Mesnil/Vair) seem to suggest that the differences are due to different maturity as consequence of different burial. Both samples come from the same geological age, Toarcian, but, Mesnil was sampled on an outcrop and Donnemarie at 2253 m depth [28]. The different aromaticity of these kerogens is also clearly reflected in their respective NMR spectra (Fig. 2).

It is apparent that significant differences exist among the different samples regarding the relative pyrolysis product concentrations, which are related to the maceral composition of the source rocks, and to a lesser extent the maturity degree of the samples. For the kerogen Types I and II, the main pyrolysis products were saturated and olefinic hydrocarbons, with minor amounts of aromatics, naphthoaromatics, organosulfur compounds, and alkylphenols, whereas aromatic compounds (alkylbenzenes and  $\text{C}_0$ – $\text{C}_2$  alkylphenols) were predominant in the Mannville kerogen (Type III).

The mass chromatograms of the *n*-alkene/*n*-alkane series (ions at  $m/z$  55 + 57) released from the different kerogens (Fig. 3) show similar chain length distributions, which contrasts with the traditional view that decreasing chain length of alkanes is related to increasing maturity [9]. However, the relative concentrations of the alkane/alkene series do not follow the expected order of  $\text{I} > \text{II} > \text{III}$ . Thus, in the Irati (I) and Mesnil (II) samples they were less abundant than in Aleksinac (I) and Donnemarie (II) samples. The dominance of the *n*-alkene/*n*-alkane series with a carbon preference index value close to unity in the Type I kerogen samples (Aleksinac and Irati) is consistent with the view that such hydrocarbons are concentrated in extremely aliphatic macerals. In the Mannville kerogen (Type III) the *n*-alkene/*n*-alkane pairs are present in lower concentrations and with different distribution, as an indication of a lower aliphatic character of this kerogen. This

observation is consistent with the chemical oxidation data, since only 14% of aliphatic acids were obtained on  $\text{KMnO}_4$  degradation for the Mannville shale, compared to 75.3% for Irati and 83.6% for Aleksinac [14,16].

## Py-GC/MS

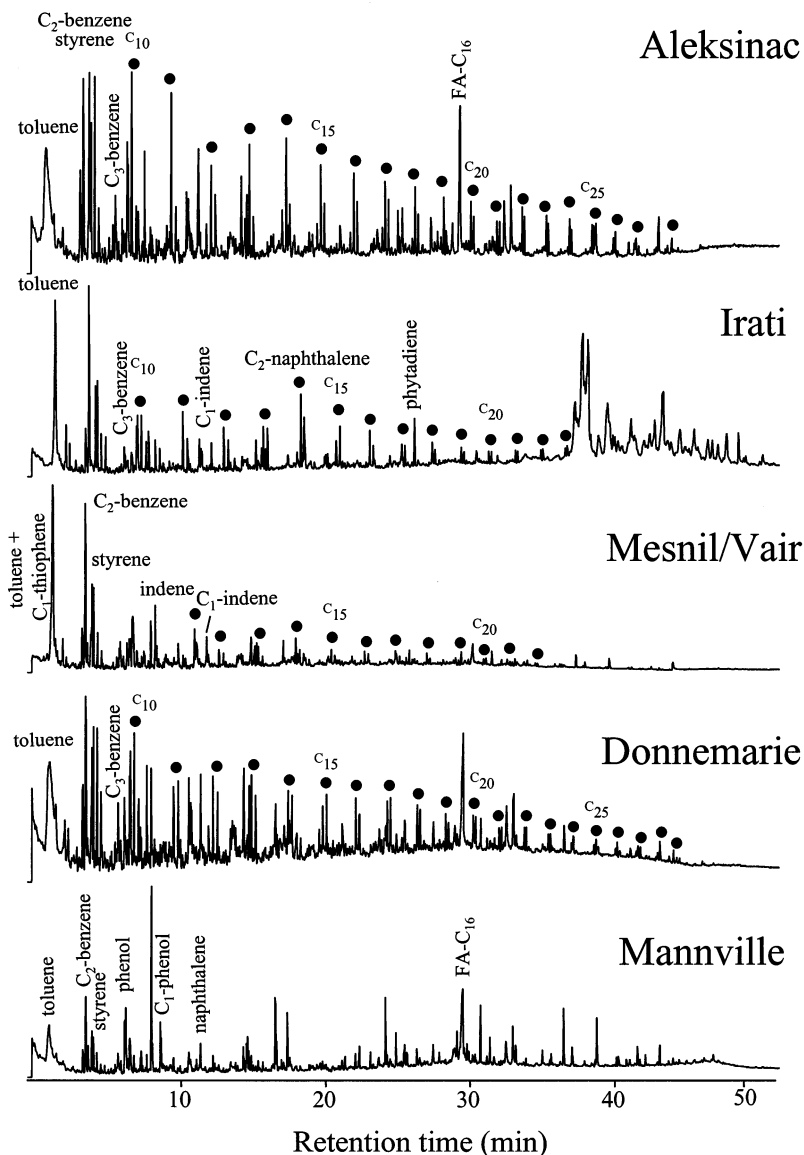


Fig. 1. Gas chromatograms of the pyrolysates (Curie-temperature 770°C) of the different kerogen samples (the symbol ● denotes the *n*-alkene/*n*-alkane doublets).

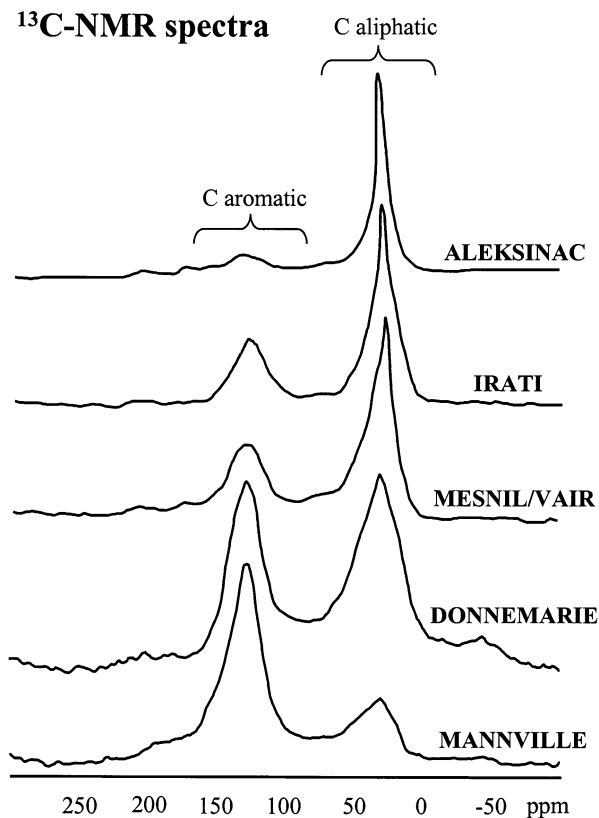


Fig. 2. CPMAS  $^{13}\text{C}$ -NMR spectra of the kerogen samples.

The distributions of the alkane/alkene pairs might indicate the presence of kerogen fractions derived from resistant non-saponifiable polyalkyl components similar to some biopolymers identified in extant and fossil plants or microbial materials [2,29,30], which could be selectively preserved during diagenesis. Ether-linked alkyl chains present in kerogen could also contribute to alkene/alkane doublets on pyrolysis. At least for the Aleksinac and Irati kerogens, their contribution is low: ether-linked alkyl chains studied using a hydrogen iodide/caesium propionate treatment revealed the presence of  $\text{C}_{14}$ – $\text{C}_{30}$  chains with dominant  $\text{C}_{16}$  (major) and  $\text{C}_{18}$  members for Aleksinac, and  $\text{C}_{12}$ – $\text{C}_{25}$  chains with dominant  $\text{C}_{16}$  and  $\text{C}_{18}$  components for Irati [31], differing significantly from the distributions given in Fig. 3.

Decarboxylation of fatty acids during pyrolysis may also be considered as another source of alkanes/alkenes [32]. Finally, linear hydrocarbons could be also released from physicochemical entrapment within the kerogen matrix by simple volatilization. This possibility was considered to explain the release of *n*-alkanes in the range  $\text{C}_{17}$ – $\text{C}_{33}$  by PTC- hydrolysis of the Aleksinac kerogen [21].

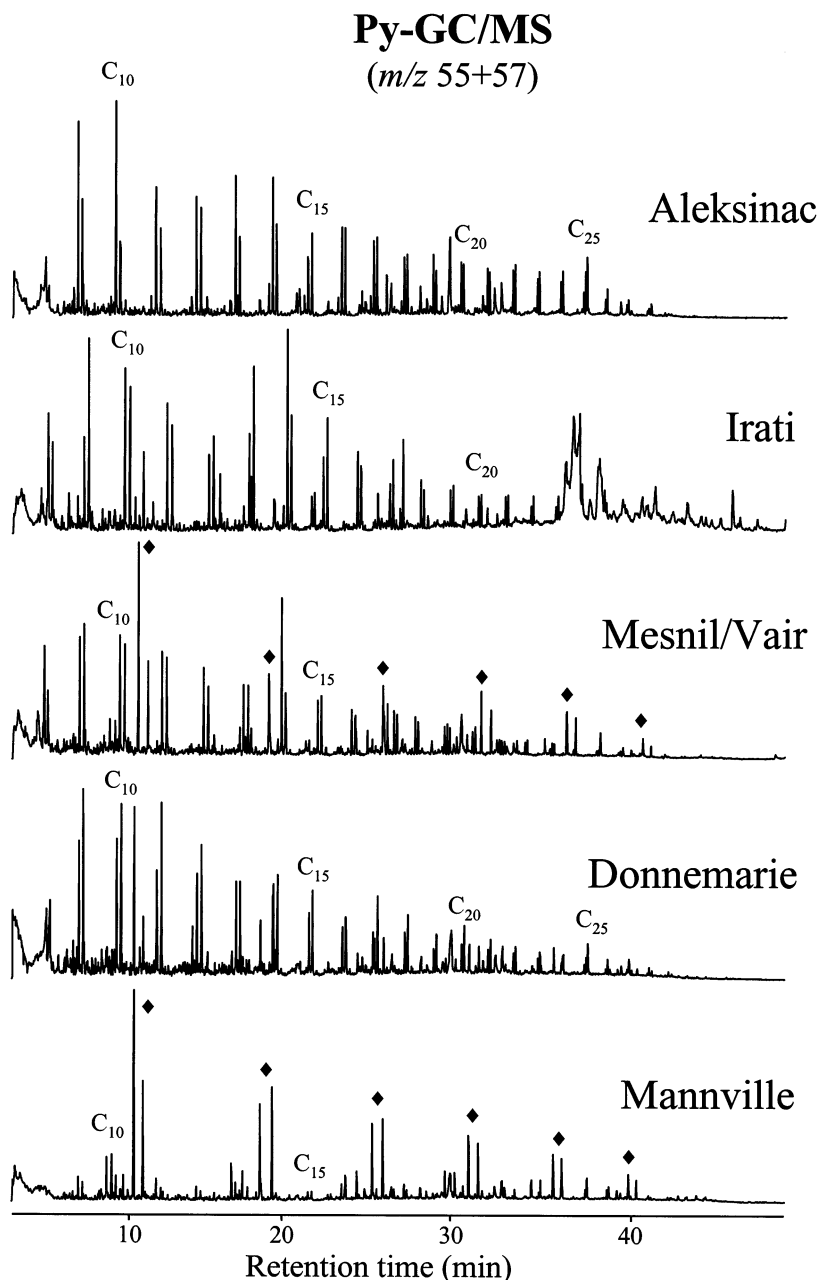


Fig. 3.  $m/z$  55 + 57 mass chromatograms showing the distribution of the  $n$ -alkane/ $n$ -alkene pairs released from the different kerogen pyrolysates (the symbol ◆ denotes a series tentatively identified as linear and/or branched alkylthiophenes).

The most prominent peaks in the pyrolysis trace of the Mannville shale kerogen in Fig. 3 correspond to a series of alkylthiophenes, exhibiting a distribution similar to those of the *n*-alkanes and *n*-alkenes. The same thiophene series was also present in the pyrolyzate of Mésnil/Vair kerogen in minor amount. Alkylthiophenes were previously reported as typical pyrolysis products from various sulfur-rich kerogens [33–38], including immature Type II kerogen from the lower Toarcian of the Paris Basin [39].

The aromatic series detected in the different conventional pyrolyzates by monitoring characteristic fragment ions are listed in Table 1, together with a semi-quantitative assessment of concentration. The relatively different proportions of aromatic products would reflect the different contributions of aromatic rich macerals to the kerogens. The data in Table 1 are in good agreement with the yields of aromatic acids released by  $\text{KMnO}_4$  degradation (Aleksinac: 7.9%; Irati: 11.1%; Toarcian shale, Paris Basin equivalent to Donnemarie: 27%; Mannville: 86%). These acids were dominantly benzenecarboxylic acids accompanied with hydroxylated benzenecarboxylic acids, and naphthalenecarboxylic acids. Various aromatic acids were also released on PTC-hydrolysis of the Irati and the Donnemarie kerogens [20,21].

Hopanoïd hydrocarbons were also identified among the pyrolysis products of Irati kerogen (Table 1) and confirmed the results of the  $\text{RuO}_4$  oxidation of this kerogen, which yielded several hopanoic acids. Because these acids were not found in the hydrolysis products, we conclude that hopanoïds were probably ether-linked to the kerogen matrix [20].

Pyrolysis in the presence of TMAH can help in the detection and identification of functionalized components, providing additional/complementary data for the structural and compositional elucidation of the kerogens. The Py/TMAH pyrograms show the presence of a series of saturated unbranched monocarboxylic acids methyl esters, as well as minor amounts of a series of hydroxy fatty acids,

Table 1

Semi-quantitative approach to the nature and relative concentrations of aromatic series detected in the pyrolyzates of the kerogen isolates

Aromatic series (Characteristic fragment ions)	AL <sup>a</sup>	IR	DO	ME	MA
C <sub>2</sub> –C <sub>4</sub> alkylated benzenes (106+120+134)	++ <sup>b</sup>	+	++	++	+++
C <sub>0</sub> –C <sub>2</sub> alkyl phenols (94+108+122)	+	+	++	+	+++
C <sub>1</sub> –C <sub>3</sub> alkyl naphthalenes (142+156+170)	+	+	++	+	+
C <sub>0</sub> –C <sub>2</sub> alkyl naphthols (144+158+172)	+	+	+	+	+
C <sub>0</sub> –C <sub>2</sub> alkylanthracenes (178+)	+	+	+	+	+
C <sub>0</sub> –C <sub>1</sub> alkyl-indenes/indanes (116+118+130+132)	+	+	++	+	+
Bicyclic alkanes (167)	–	++	–	–	–
Steranes ( $\alpha$ , $\beta$ , 4Me-) (217+218+231)	+	+	–	–	+
Hopanes/benzohopanes (191)	–	++	–	–	–
C <sub>0</sub> –C <sub>2</sub> alkylpyrenes/benzopyrene	–	+++	–	–	–

<sup>a</sup> AL: Aleksinac, IR: Irati, DO: Donnemarie, ME: Mésnil/Vair, MA: Mannville.

<sup>b</sup> +, ++, +++: low, moderate and high abundances; –: non detected.



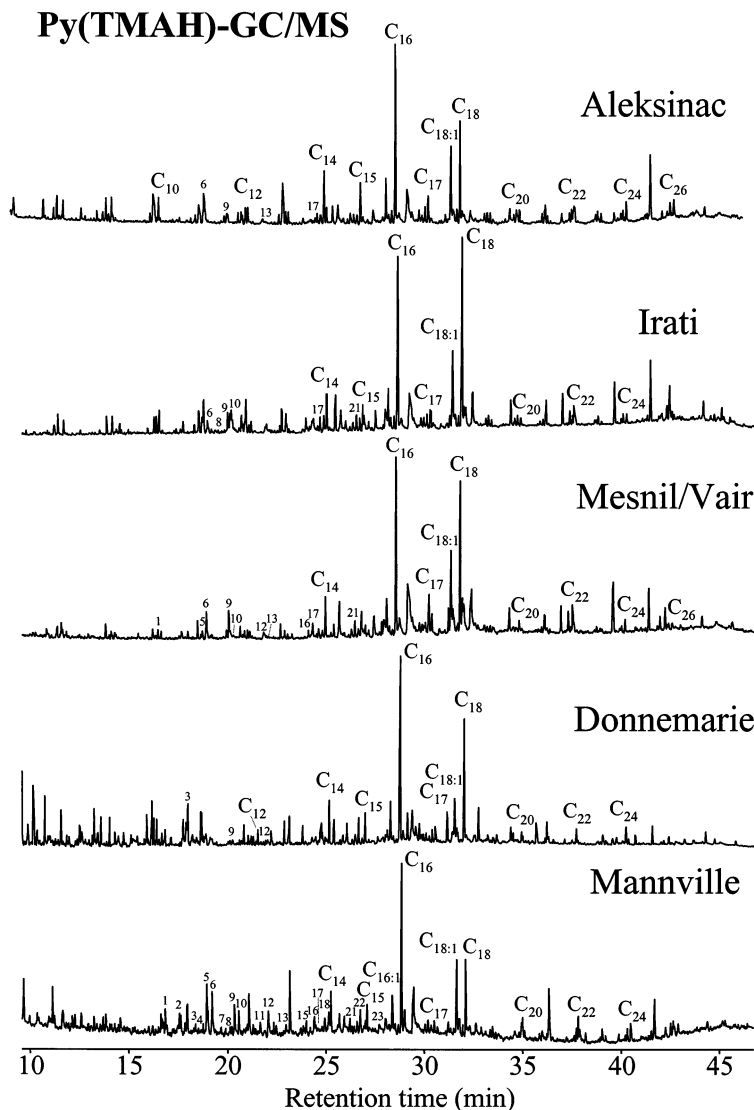


Fig. 4. Total ion chromatograms of the Py/TMAH pyrolysates.  $C_n$  correspond to the series of fatty acid methyl esters. Numbers refer to the compounds listed in Table 2.

$\alpha,\omega$ -dicarboxylic acids and benzenecarboxylic acids, as methyl esters (Fig. 4). Table 2 shows the aromatic compounds (benzenecarboxylic acids and lignin-derived fragments) released upon Py/TMAH, which were not previously detected upon conventional pyrolysis. Benzenecarboxylic acids were also identified in substantial amounts after chemical degradations of the studied kerogens [16,20,21].

The aliphatic acid series might derive from acids linked to the macromolecular network via sterically protected, and hence, non-hydrolyzable ester bonds [26] and

may be inherited directly from living organisms into kerogens at an early stage of sedimentation [40]. Although fatty acids have been often detected in kerogen pyrolysates [41], their probably high contribution to the structure of kerogens has been underestimated, because upon conventional pyrolysis they undergo decarboxylation and are not observed as acids. Some authors [42,43] noticed that, in conventional pyrolysis, fatty acids and aliphatic dicarboxylic acid moieties present in the structure of humic substances decarboxylate, producing various series of alkanes, alkenes and alkylbenzenes. The use of pyrolysis in the presence of TMAH avoids decarboxylation by protecting the carboxyl groups and releases them as methyl esters. Large quantities of fatty acids (as methyl esters) have also been released from other kerogens [12,26] and humic substances [44–46] by this procedure. Therefore, the use of pyrolysis–methylation seems to corroborate the presence of fatty acid moieties in the kerogen structure. It is obvious that pyrolysis–methylation provides complementary information to that obtained by conventional pyrolysis about the structure of these materials.

The distribution of the series of monocarboxylic acids methyl esters (FAMES) ( $m/z$  74 mass chromatograms) released from the different kerogens by Py/TMAH is shown in Fig. 5. An even carbon number predominance in the range  $C_6$ – $C_{26}$  and maxima at  $C_{16}$  and  $C_{18}$  were observed in all cases. *Iso*- and *anteiso*- $C_{15}$  and  $C_{17}$

Table 2

Aromatic compounds identified in the different samples after Py(TMAH)–GC/MS

No.	Compound
1	3-methoxybenzenecarboxylic acid, methyl ester
2	4-methoxybenzenecarboxylic acid, methyl ester
3	1,3,5-trimethoxybenzene
4	3,4,5-trimethoxytoluene
5	4-methoxybenzeneacetic acid, methyl ester
6	benzenedicarboxylic acid, dimethyl ester
7	methoxybenzeneacetic acid, methyl ester
8	trimethoxytoluene
9	benzenedicarboxylic acid, dimethyl ester
10	benzenedicarboxylic acid, dimethyl ester
11	<i>cis</i> -1-(3,4-dimethoxyphenyl)-3-methoxyprop-1-ene
12	3,4-dimethoxybenzenecarboxylic acid, methyl ester
13	<i>trans</i> -1-(3,4-dimethoxyphenyl)-3-methoxyprop-1-ene
14	methoxybenzenedicarboxylic acid, dimethyl ester
15	trimethoxybenzenecarboxylic acid, methyl ester
16	methoxybenzenedicarboxylic acid, dimethyl ester
17	3,4,5-trimethoxybenzenecarboxylic acid, methyl ester
18	methoxybenzenedicarboxylic acid, dimethyl ester
19	methoxybenzenedicarboxylic acid, dimethyl ester
20	1-(3,4-dimethoxyphenyl)-1,3-dimethoxyprop-1-ene
21	benzenetricarboxylic acid, trimethyl ester
22	benzenetricarboxylic acid, trimethyl ester
23	benzenetricarboxylic acid, trimethyl ester

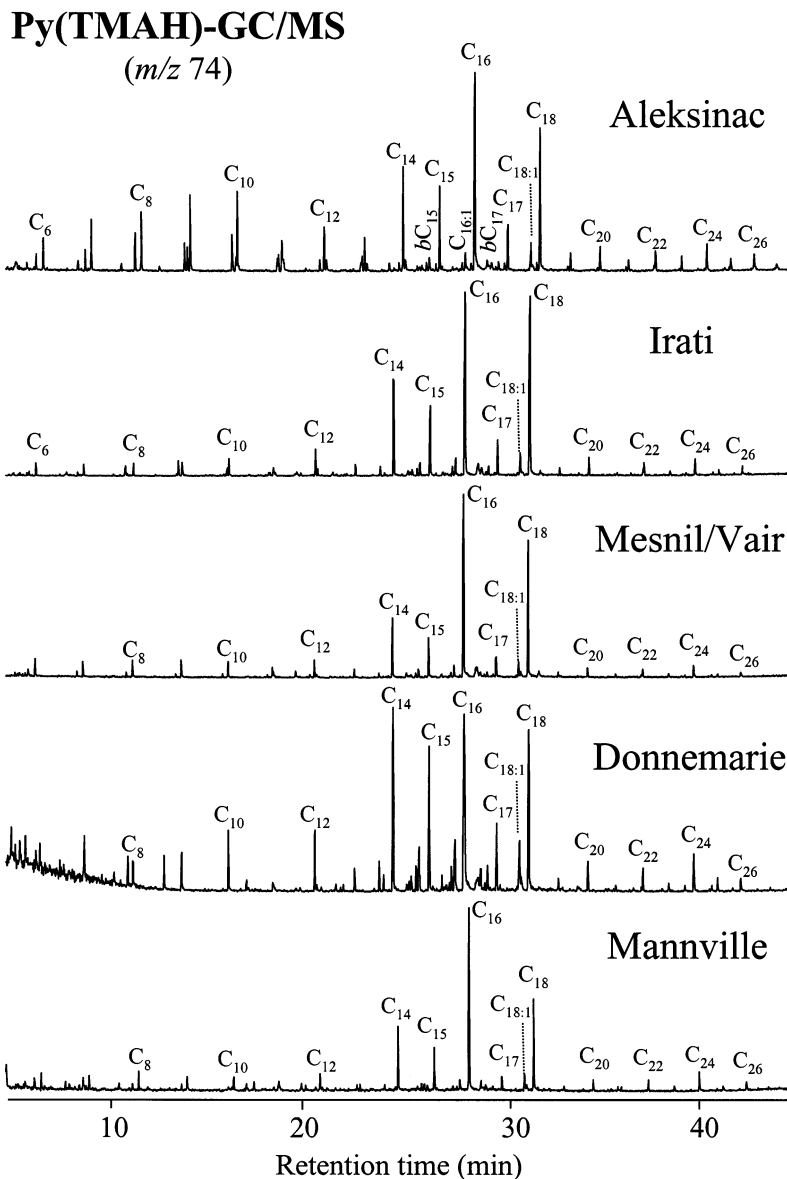


Fig. 5.  $m/z$  74 mass chromatograms showing the distribution of fatty acid series (as methyl esters) released after the pyrolysis-methylation of the different kerogens.

fatty acids, characteristic of bacterial contributions, were also detected among the released compounds. Small amounts of unsaturated C<sub>18:1</sub> and C<sub>16:1</sub> fatty acids were also released from all the kerogens studied here. These unsaturated moieties may have been incorporated and preserved into the kerogen network. It appears,

therefore, that an important preservation due to the occurrence of esterified monocarboxylic acids occurred not only in the immature kerogens but also in more mature kerogen concentrates. Similar distributions were observed by Py/TMAH of other kerogens [26,47], but also somewhat different. Kralert et al. [12] reported the release of fatty acids in the range  $C_6$ – $C_{32}$ , with the lower homologues ( $< C_{20}$ ) presumed to be algal in origin, whereas, for the  $C_{24}$ – $C_{30}$  acids, a higher plant source has been postulated [48]. In the case of the Irati shale the result is consistent with its assignments as algal/microbial kerogen [49].

These series of aliphatic acids could also arise from the higher plant cutin and perhaps suberin residues, which could be chemically bound to the kerogen macromolecule through ester linkages. These biopolyesters are relatively stable against geochemical transformations and may be selectively preserved in the macromolecular matrix of the kerogen. These ester-bound fatty acids seem to be protected in the most refractory part of the macromolecular network, and hence would survive diagenetic degradation [26].

Although differences in mass spectral response factors (typical for ion trap mass analyzers) discriminate against the high molecular species, the distribution of FAMES compares well with that reported for long-chain carboxylic acids produced by  $KMnO_4$  degradation of Irati, Aleksinac, and Mannville kerogens [14,15,17]. On  $RuO_4$  oxidation of Irati kerogen, the distribution of  $C_9$ – $C_{32}$  aliphatic monocarboxylic acids was highly dominated by the  $C_{16}$  component [20]. The same distribution of fatty acids given in Fig. 5 was found after PTC-hydrolysis of Irati and Aleksinac kerogens [19,20], which afforded linear  $C_{12}$ – $C_{20}$  monocarboxylic acids with major  $C_{16}$  and  $C_{18}$  members accompanied with short  $C_7$ ,  $C_9$  and  $C_{10}$  components. In the Donnemarie kerogen, esterified linear monocarboxylic acids are present in the range  $C_{14}$ – $C_{31}$  with major  $C_{16}$  and  $C_{18}$  components.

#### 4. Conclusions

From the results obtained two main conclusions can be drawn: (a) the different proportions and distributions of the main pyrolysis products released from the different kerogens (dominated by saturated and olefinic hydrocarbons, aromatics and naphthoaromatics, alkyl phenols, organosulfur compounds and carboxylic acids) enable structural differentiation among the samples; (b) Py/TMAH allowed additional/complementary identification of functionalized pyrolysis products which reflect structural and compositional characteristics of the parent material. In general, the data demonstrate that Py/TMAH provides relatively good preservation of the original carboxylic moieties present in the macromolecular structure of kerogens owing to protection of the functional groups from thermal reactions. The chemical structures of the released products (mainly saturated and unsaturated unbranched mono- and dicarboxylic acids were identified as their methyl esters in all the samples) were similar to those found by PTC-hydrolysis of the studied kerogens. Therefore both Py/TMAH and PTC-hydrolysis data indicate that considerable amounts of functionalized compounds are bound to the macromolecular structure via ester and ether linkages.

The pyrolytic and oxidative approaches seem to be, up to now, complementary. Py/TMAH is a good analytical tool to study functionalized moieties in the kerogen structure. As many possibilities of molecular arrangements often exist to explain the results, more detailed structural information about the complex forms of organic matter requires, at the moment, the use of selective chemical degradation.

## References

- [1] B.P. Tissot, D.H. Welte, *Petroleum Formation and Occurrence*, 2nd edn, Springer, Heidelberg, 1984, p. 699.
- [2] E.W. Tegelaar, J.W. De-Leeuw, S. Derenne, C. Largeau, *Geochim. Cosmochim. Acta* 53 (1989) 3103.
- [3] J. Rullkötter, W. Michaelis, *Org. Geochem.* 16 (4-6) (1990) 829.
- [4] J.K. Whelan, C. Thompson-Rizer, Chemical methods for assessing kerogen and proto-kerogen types and maturity, in: M. Engel, S. Macko (Eds.), *Organic Geochemistry*, Plenum Press, New York, 1993, p. 289.
- [5] S.R. Larter, A.G. Douglas, in: A.G. Douglas, J.R. Maxwell (Eds.), *Advances in Organic Geochemistry*, Pergamon Press, Oxford, 1979, p. 579.
- [6] S.R. Larter, in: K.E. Voorhees (Ed.), *Analytical pyrolysis. Techniques and Applications*, Butterworths, London, 1984, p. 212.
- [7] S.R. Larter, J.T. Senftle, *Nature* 318 (1985) 277.
- [8] B.S. Horsfield, in: J. Brooks, D. Welte (Eds.), *Advances in Petroleum Geochemistry*, vol. 1, Academic Press, London, 1984, p. 247.
- [9] B.S. Horsfield, *Geochim. Cosmochim. Acta* 53 (1989) 891.
- [10] S.R. Larter, B. Horsfield, in: M. Engel, S. Macko (Eds.), *Organic Geochemistry*, Plenum Press, New York, 1993, p. 271.
- [11] M.A. Gohi, T. Eglinton, *J. High Res. Chrom.* 17 (1994) 476.
- [12] P.G. Kralert, R. Alexander, R.I. Kagi, *Org. Geochem.* 23 (1995) 627.
- [13] P.F. Greenwood, N. Sherwood, G.D. Willett, *J. Anal. Appl. Pyrol.* 31 (1995) 177.
- [14] A. Amblès, M. Djordjevic, D. Vitorovic, *Chem. Geol.* 48 (1985) 305.
- [15] D. Vitorovic, S. Bajc, A. Amblès, *Croatica Chemica Acta* 58 (1985) 453.
- [16] D. Vitorovic, A. Amblès, S. Bajc, O. Cvetkovic, P. Polic, *J. Serb. Chem. Soc.* 59 (2) (1994) 75.
- [17] D. Vitorovic, M. Djordjevic, A. Amblès, J.C. Jacquesy, *AOSTRA J. Res.* 3 (1987) 163.
- [18] A. Amblès, N. Baudet, J.C. Jacquesy, A. Kribii, *Tetrahedron Letters* 33 (1992) 5193.
- [19] A. Amblès, N. Baudet, J.C. Jacquesy, *Tetrahedron Letters* 34 (1993) 1783.
- [20] A. Kribii, N. Baudet, A. Amblès, *J. Serb. Chem. Soc.* 61 (1996) 959.
- [21] A. Amblès, L. Grasset, G. Dupas, J.C. Jacquesy, *Org. Geochem.* 24 (1996) 681.
- [22] J.M. Challinor, *J. Anal. Appl. Pyrolysis* 29 (1994) 223.
- [23] J.C. del Río, F. Martin, F.J. González-Vila, *Trends Anal. Chem.* 15 (1996) 70.
- [24] F.J. González-Vila, J.C. Del-Río, F. Martin, T. Verdejo, *J. Chromatogr. A* 750 (1996) 155.
- [25] J.M. Challinor, *J. Anal. Appl. Pyrolysis* 20 (1991) 15.
- [26] J.C. del Río, F. Martin, F.J. Gonzalez-Vila, T. Verdejo, *Org. Geochem.* 23 (11/12) (1995) 1009.
- [27] R. Fründ, H.-D. Lüdemann, *Sci. Total Environ.* 81/82 (1989) 157.
- [28] N. Brach-Labsir, *Etude structurale des kérogènes par réactions non dégradatives*. PhD thesis Dissertation, University of Poitiers, September 1991.
- [29] C. Largeau, S. Derenne, E. Casadevall, N. Sellier, in: D. Leythausen, J. Rullkötter (Eds.), *Advances in Organic Geochemistry*, Pergamon Press, Oxford, 1985, p. 1985.
- [30] J.W. de Leeuw, P.F. van Bergen, B.G.K. van Aarssen, J.P.L.A. Gatellier, J.S. Sinninghe Damsté, M.T. Collison, *Phil. Trans. R. Soc. Lond. B* 333 (1991) 329.
- [31] A. Grasset, A. Amblès, *Anal. Chem.*, in press.
- [32] W.A. Hartgers, J.S. Sinninghe-Damsté, J.W. de Leeuw, *J. Anal. Appl. Pyrolysis* 34 (1995) 191.

- [33] J.S. Sinningue-Damste, A.C. Rock-Van Dalen, J.W. de Leeuw, P.A. Schenck, J. Chromatogr. 435 (1988) 435.
- [34] C. Vallejos, S. Talukdar, R.P. Philp, Energy Fuels 3 (1989) 366.
- [35] M. Ishiwatari, H. Sakashita, T. Tatsumi, H. Tominaga, J. Anal. Appl. Pyrolysis 17 (1990) 217.
- [36] T. Eglinton, J.S. Sinningue-Damste, M.E. Kohnen, J.W. de Leeuw, Fuel 69 (1990) 1394.
- [37] M.P. Koopmans, J.S. Sinningue-Damste, M.D. Lewan, J.W. de Leeuw, Org. Geochem. 23 (1995) 583.
- [38] S. Svel-Cerovecki, I. Eskinja, A. Alajbeg, J. Anal. Appl. Pyrolysis 34 (1995) 143.
- [39] M.A. Kruger, P. Landais, D.F. Bensley, B.A. Stankiewicz, M. Elie, O. Ruau, Energy Fuels 11 (1997) 503.
- [40] K. Kawamura, R. Ishiwatari, Org. Geochem. 8 (1985) 197.
- [41] J. Connan, in: B. Tissot, F. Biennier (Eds.), Advances in Organic Geochemistry, Editions Technip, Paris, 1973, p. 73.
- [42] C. Saiz-Jimenez, Environ. Sci. Technol. 28 (11) (1994) 1773.
- [43] F. Martín, F.J. González-Vila, J.C. del Río, T. Verdejo, J. Anal. Appl. Pyrol. 28 (1994) 71.
- [44] P.G. Hatcher, D.J. Clifford, Org. Geochem. 21 (1994) 1081.
- [45] J.C. del Río, F.J. González-Vila, F. Martín, T. Verdejo, Org. Geochem. 22 (1994) 885.
- [46] F. Martín, J.C. del Río, F.J. González-Vila, T. Verdejo, J. Anal. Appl. Pyrol. 31 (1995) 75.
- [47] K. Kawamura, E. Tannenbaum, B.J. Huizinga, I.R. Kaplan, in: D. Leythausen, J. Rullkötter (Eds.), Advances in Organic Geochemistry, Pergamon Press, London, 1985.
- [48] A.D. Barakat, Energy Fuels 7 (1993) 988.
- [49] J.C. Afonso, M. Schmal, J.N. Cardoso, Fuel 73 (1994) 363.